Structure and formation mechanism of the E'_α center in amorphous SiO$_2$

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We provide a possible formation mechanism for one of the Si-related paramagnetic centers in amorphous silica, E'_α, which is stable only below 200 K, on the basis of the quantum-chemical calculations. We show that the divalent Si defect can trap a hole, resulting in two different types of paramagnetic centers that are consistent with the experimental spectral features for E'_α. The highly anisotropic symmetry and the isotropic hyperfine coupling constants observed for one of the E'_α-center variants are reproduced by the present model. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1369147]

It is accepted that the photosensitivity of amorphous silicon dioxide (a-SiO$_2$) is closely related to the nature of intrinsic point defects that can be transformed into other defect species during the irradiation process.[1] Furthermore, point defects, both intrinsic and photoinduced forms, result in the degradation of the optical properties of the silicon-based materials such as fiber waveguides and metal–oxide–semiconductor devices. Thus point defects in a-SiO$_2$ have been the subjects of intense research although their structure and generation mechanism are still a matter of controversy.

The most widely investigated point defect in a-SiO$_2$ is the so-called ''E' center,'' which can be best characterized by electron spin resonance (ESR) signals.[2] The generic model of the E' center is an unpaired spin in a dangling tetrahedral orbital of a three-coordinated silicon atom, i.e., $\equiv$ Si·, where ''$\equiv$'' denotes the three Si–O bonds and ''·'' represents the unpaired electron. It has been established that in a-SiO$_2$ there exists at least four distinguishable Si-relaxed paramagnetic centers (E'_γ, E'_α, E'_β, and E'_δ).[3,4] However, the nature of the E'_α center is less certain as compared with the other E'-center variants, and at present there exists no plausible model to account for the observed ESR characteristics for the E'_α center.[4–6] Thus, the aim of this letter is to provide a possible model of the E'_α center on the basis of quantum-chemical calculations.

Griscom[7] has shown that the E'_α center is stable only below ~200 K, suggesting a transient nature of this defect. Griscom[7] has also demonstrated that two variants of E'_α are present: $E'_{\alpha 1}$ and $E'_{\alpha 2}$, characterized by extreme anisotropic symmetry and ''near axial'' symmetry, respectively (see Table I). It has been found that the $E'_{\alpha 1}$ center, which is generated on x-ray irradiation at 77 K, is converted into the $E'_{\alpha 2}$ center after exposure to room light. This result indicates that the latter center is more energetically favorable than the former one.

Previously, it has been generally assumed that possible precursors of the E'-center variants are the oxygen monovacancy and/or its related defect center.[4–10] As for E'_α, however, it would be difficult to give a reasonable structural model in terms of this assumption. Thus, in this letter, we employ the divalent Si defect instead of the oxygen mono-

vacancy as a candidate for the precursor of E'_α. The divalent Si, which yields the optical absorption band at ~5.0 eV,[11] can be viewed as a twofold coordinated Si, and therefore, it is possible that this oxygen-deficiency center (ODC) is also responsible (although partially) for the paramagnetic forms of ODCs such as E' centers upon irradiation. Recently, Skuja[12] indeed suggested that the divalent defect is subject to structural rearrangement upon ionizing irradiation or trapping of a hole on the defect.

Figure 1 shows the Si$_{14}$O$_{18}$H$_{18}$ cluster, termed model 1, used to model the divalent Si defect embedded in the SiO$_2$ framework. The ''surface'' silicon atoms in the cluster were terminated by hydrogen atoms to saturate the dangling bonds. The geometry of model 1 was optimized at the Hartree–Fock (HF) level without imposing any structural constraints using the 6-31G(d) basis set.[13] We then fully reoptimized the geometry of model 1 at the unrestricted HF (UHF)/6-31G(d) level by assuming a total charge of $+1$ to simulate an ionizing irradiation process. All *ab initio* MO calculations in this work have been performed with the GAUSSIAN-98 program.[14]

If we simply assume a total charge of $+1$ for model 1, we obtained the configuration termed model 2 [see Fig. 2(a)]. In model 2, the divalent Si (Si1) traps a positive hole and attracts a nearby bridging oxygen atom (O2) to form a structural unit having one three-coordinated silicon (Si1) and one three-coordinated oxygen (O2) atoms. These calculated results allow us to suggest that when one of the lone pair of electrons on the divalent Si defect is excited to the conduction band, the silicon sp^2 hybrid orbitals on the two-coordinated center will be relaxed into the sp^3-like ones by attracting a nearby bridging oxygen atom, resulting in the

TABLE I. Observed (Ref. 4) and calculated spin Hamiltonian parameters for the E_α variants in amorphous silica.

Center	g_1	g_2	g_3	A (mT) Obs.	A (mT) Calc.
$E'_{\alpha 1}$	2.0018	2.0013	1.9998	42	43.91[a]
$E'_{\alpha 2}$	2.0018	2.0006	2.0003	42	42.63[b]

[a]Calculated value for Si$_{(1)}$ in model 2 at the UHF/6-31G(d) level.
[b]Calculated value for Si$_{(1)}$ in model 3 at the UHF/6-31G(d) level.
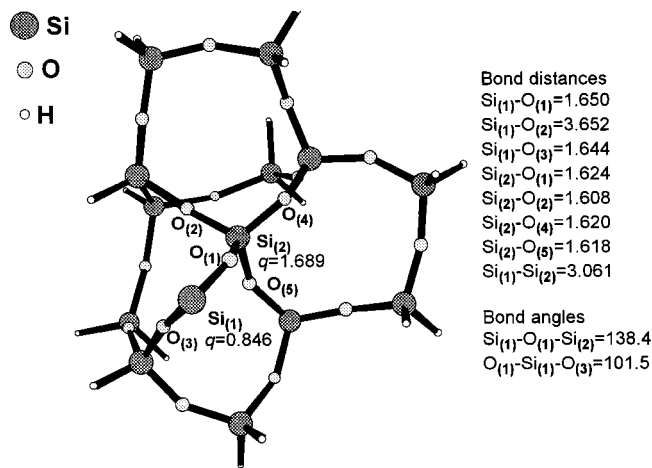
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Si
O
H

Bond distances
$Si_{(1)}$-$O_{(1)}$=1.650
$Si_{(1)}$-$O_{(2)}$=3.652
$Si_{(1)}$-$O_{(3)}$=1.644
$Si_{(2)}$-$O_{(1)}$=1.624
$Si_{(2)}$-$O_{(2)}$=1.608
$Si_{(2)}$-$O_{(4)}$=1.620
$Si_{(2)}$-$O_{(5)}$=1.618
$Si_{(1)}$-$Si_{(2)}$=3.061

Bond angles
$Si_{(1)}$-$O_{(1)}$-$Si_{(2)}$=138.4
$O_{(1)}$-$Si_{(1)}$-$O_{(3)}$=101.5

$O_{(2)}$ $O_{(4)}$
$O_{(1)}$ $Si_{(2)}$
$q=1.689$
$O_{(5)}$
$Si_{(1)}$
$O_{(3)}$ $q=0.846$

FIG. 1. Structure of the $Si_{14}O_{18}H_{18}$ cluster including the divalent Si defect (model 1) optimized at the HF/6-31G(d) level. Principal bond distances and bond angles are shown in Å and degrees, respectively. Mulliken atomic charges q are also shown.

three-coordinated Si site. It should also be noted that the spin density of Si1 in model 2 is calculated to be 0.915, indicating an unpaired electron in model 2 is almost localized at the newly formed three-coordinated silicon site. We have also found that model 2 can further relax into the configuration termed model 3 [see Fig. 2(b)], which is lower in total energy than model 2 by 0.63 eV. This structural transformation is accomplished just by breaking the Si2–O2 bond in model 2, resulting in two different three-coordinated silicon sites (Si1 and Si2) in model 3. In model 3, the unpaired spin ρ is almost localized at one of the three-coordinated silicons, Si1 ($\rho_{Si1}=0.928$), and therefore, the rest of the three-coordinated silicon (Si2) can be regarded as the hole-trapping center ($\equiv Si2^+$). The isotropic hyperfine splittings for Si1 in models 2 and 3 are calculated to be 43.9 and 42.6 mT, respectively, which are in agreement with the observed values for E'_α (see Table I).

It should also be worth mentioning that model 2 is capable of explaining the strong anisotropy observed for $E'_{\alpha1}$. As shown in Fig. 2(a), the paramagnetic part of the defect ($\equiv Si1\cdot$) in model 2 has an anisotropic configuration; the Si–O bond distances in this structural unit range from ~ 1.58 to ~ 1.80 Å. Such an anisotropy is inherent in the fact that one of the consisting oxygen atoms in the $\equiv Si1\cdot$ unit is a three-coordinated oxygen. On the other hand, the $\equiv Si1\cdot$ unit in model 3 has similar Si–O bond distances (1.608, 1.657, and 1.655 Å), explaining near axial symmetry for $E'_{\alpha2}$. It should also be noted that the defect in model 3, in which the $\equiv Si1\cdot$ and $\equiv Si2^+$ units are bridged by a common oxygen atom (O1), is similar to the defect model we have recently proposed as a model of the E'_γ center although the formation mechanism of the latter center is different from the present case.[10]

In summary, we have shown that the divalent Si defect (model 1) can transform into two different types of paramagnetic centers (models 2 and 3) by trapping a hole. The conversion from model 1 to models 2 and 3 is accomplished without accompanying complex atomic rearrangements, suggesting that the present structural transformation among these defect centers is possible to occur upon ionizing irradiation even at low temperature. The paramagnetic defect in
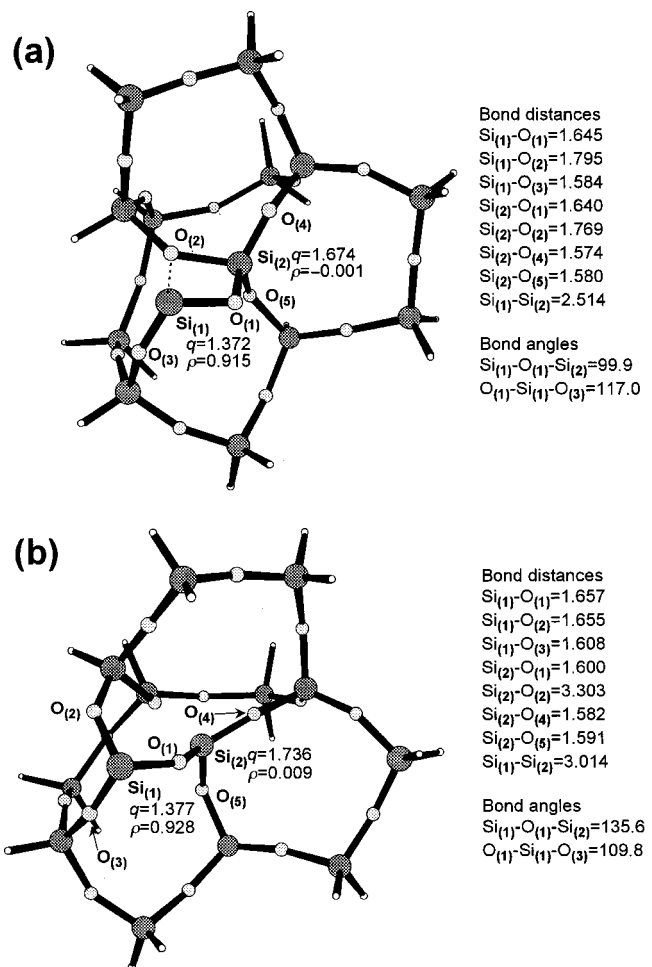
(a)

Bond distances
$Si_{(1)}$-$O_{(1)}$=1.645
$Si_{(1)}$-$O_{(2)}$=1.795
$Si_{(1)}$-$O_{(3)}$=1.584
$Si_{(2)}$-$O_{(1)}$=1.640
$Si_{(2)}$-$O_{(2)}$=1.769
$Si_{(2)}$-$O_{(4)}$=1.574
$Si_{(2)}$-$O_{(5)}$=1.580
$Si_{(1)}$-$Si_{(2)}$=2.514

Bond angles
$Si_{(1)}$-$O_{(1)}$-$Si_{(2)}$=99.9
$O_{(1)}$-$Si_{(1)}$-$O_{(3)}$=117.0

$O_{(2)}$ $O_{(4)}$
$Si_{(2)}$ $q=1.674$
$\rho=-0.001$
$Si_{(1)}$ $O_{(1)}$ $O_{(5)}$
$q=1.372$
$O_{(3)}$ $\rho=0.915$

(b)

Bond distances
$Si_{(1)}$-$O_{(1)}$=1.657
$Si_{(1)}$-$O_{(2)}$=1.655
$Si_{(1)}$-$O_{(3)}$=1.608
$Si_{(2)}$-$O_{(1)}$=1.600
$Si_{(2)}$-$O_{(2)}$=3.303
$Si_{(2)}$-$O_{(4)}$=1.582
$Si_{(2)}$-$O_{(5)}$=1.591
$Si_{(1)}$-$Si_{(2)}$=3.014

Bond angles
$Si_{(1)}$-$O_{(1)}$-$Si_{(2)}$=135.6
$O_{(1)}$-$Si_{(1)}$-$O_{(3)}$=109.8

$O_{(2)}$ $O_{(4)}$
$O_{(1)}$ $Si_{(2)}$ $q=1.736$
$\rho=0.009$
$Si_{(1)}$ $O_{(5)}$
$q=1.377$
$\rho=0.928$
$O_{(3)}$

FIG. 2. Optimized geometries of the $(Si_{14}O_{18}H_{18})^+$ clusters calculated at the UHF/6-31G(d) level: (a) model 2, (b) model 3. The total energy of model 2 is higher than that of model 3 by 0.63 eV. Principal bond distances and bond angles are shown in Å and degrees, respectively. Mulliken atomic charges q and spin densities ρ are also shown.

the higher energy form of the positively charged cluster (model 2) is characterized by a very anisotropic configuration, whereas the corresponding defect in the lower energy form (model 3) by near axial symmetry. We suggest that these two different paramagnetic defects derived originally from the divalent Si defect account for the experimental ESR characteristics for the two E'_α variants, namely, $E'_{\alpha1}$ and $E'_{\alpha2}$.

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